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CHANGE IN THE STRUCTURE OF FIRED GLASS ENAMELS WITH DIFFERENT IRON OXIDE CONTENT

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The structures of enamels with different iron oxide content are investigated. It is shown that the structure changes with increasing iron oxide concentration. The elevated mobility of silicon-oxygen groupings surrounded by iron cations gives rise to the restructuring of the groupings into a crystalline phase possessing minimum energy.

Key words: structure, glass enamel, surface tension, crystallization, IR spectra, vibrations, structural changes, iron oxide, infrared radiation, thermocapillary motion, gaseous inclusions, amorphous halo, x-ray phase analysis.

In studying the physical and chemical properties of melts of enamel frits it has been found that the curves of the surface tension versus the composition, calculated theoretically by Dietzel's method, are rectilinear while the curves constructed according to the experimental data are extremal [1]. The appearance of a minimum in the content range 8 – 10 wt.% Fe_2O_3 is apparently due to a structural rearrangement of the melt and subsequent crystallization. In the present work structural studies of enamels with different content of iron oxides were performed in order to explain the properties of enamel melts. The increase in the concentration of iron oxides in the near-contact layer of ground-coat enamel is a consequence of exchange reactions occurring during firing with the participation of bonding oxides.

The IR spectra of samples of GK-331 enamels with different iron oxide Fe_2O_3 content are displayed in Fig. 1. The compositions presented neglect the initial Fe_2O_3 content in the enamel frit, comprising about 1% (mass fraction).

The principal minimum of the curves, which corresponds to the wave number 1000 cm^{-1}, is due to the vibrations in the structural link Si–O. The change in the positions of the transmission minima at the corresponding wave numbers is due to the structural features of the polyhedron $[SiO_4]^{4-}$. Apparently, iron oxide in enamel acts like a modifier. In the absence or low content of Fe_2O_3 the tetrahedron $[SiO_4]^{4+}$ is relative strong. For iron oxide high content the cations Fe^{2+} and Fe^{3+} reside near the oxygen vertices of the tetrahedron, closing on themselves the valence bonds of the oxygen atoms. As a result these vertices lose bonding with the silicon-oxygen framework. In consequence, the capability of individual links of the groupings SiO_4 to undergo vibrational motions increases. The curve *1* refers to the initial enamel without added iron oxide; all subsequent curves reflect the increased Fe_2O_3 content. An increase in the mass fraction of

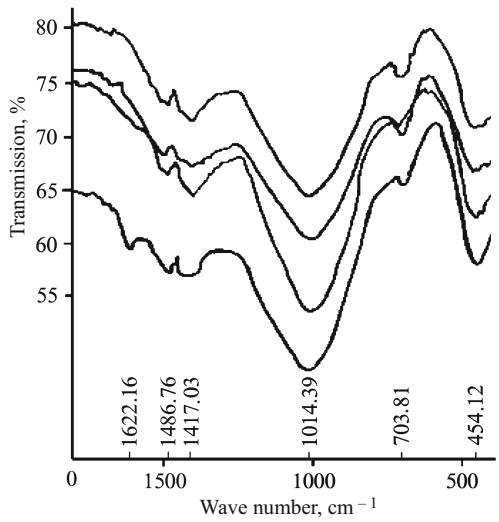

Fig. 1. IR spectra of GK-331 enamel with different content (by weight) of additionally added Fe_2O_3: *1*) 1014.39 cm^{-1} (no added Fe_2O_3); *2*) 1005.20 cm^{-1} (9% Fe_2O_3); *3*) 1000 cm^{-1} (12% Fe_2O_3); *4*) 996.95 cm^{-1} (15% Fe_2O_3).

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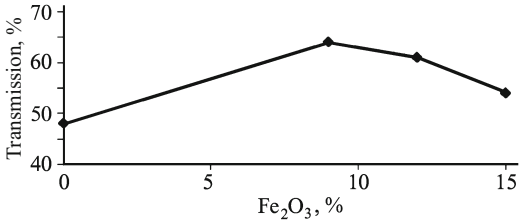

Fig. 2. IR transmission of enamels versus the added Fe_2O_3 content (by weight) for wave number near the principal minimum.

iron oxide Fe_2O_3 gives rise to the local extrema observed in the curves *2 – 4*.

The temperature difference between the outer and inner surfaces of the glass enamel melt depends on the ability of the enamel layer to transmit or block infrared radiation during firing. This temperature difference gives rise to, specifically, thermocapillary motion of gas inclusions in the enamel layer [2].

The transmission of IR waves is largely regulated by the composition of the enamel. It is known that the enrichment of the ground-coat enamel by iron oxides as a result of the contact interaction with the metal can lead to the appearance of 'copper' spots. The phase separation affects the positions and shapes of the lines in the IR spectrum. If it were not for the fact that an increase in the iron oxide Fe_2O_3 concentration gives rise to structural changes, the lines in the spectrum would shift proportionally to the concentration. The appearance of interphase boundaries sharply lowers the transmittance of the melt, as a result of which the curves *3* and *4* move down relative to the curve *2* (Fig. 2). This fact is confirmed by observations of 'copper head' defects in enameling technology. In the literature the appearance of such defects is usually attributed to the presence of iron oxide Fe_2O_3 in melt at elevated Fe_2O_3 concentrations to 10 – 15%.

If a relatively large temperature difference is characteristic for the first sample, then the temperature drop will be much smaller for the second sample. Therefore, the contribution of the thermocapillary motion to the total displacement of the bubbles will be larger in the first case.

One of the main methods of detecting a crystalline phase is x-ray phase analysis. The appearance of crystals of different nature in a crystal lattice is quite simple to record.

Apparently, a segregation of microcrystals in the glass matrix of silicate melt changes the form of the amorphous halo somewhat.

A plot of the x-ray phase analysis of samples of GK-331 enamel with different Fe_2O_3 content is presented in Fig. 3. This plot was obtained at the Institute of High-Temperature

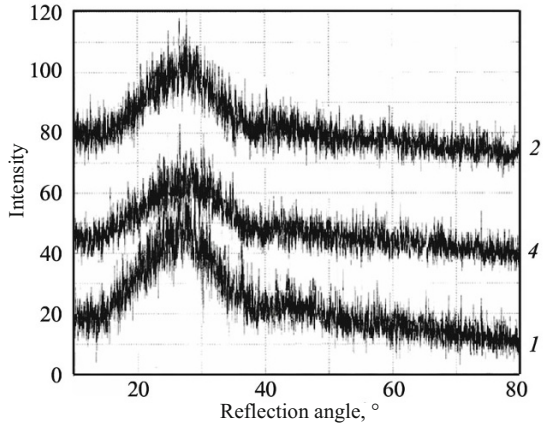

Fig. 3. X-ray phase analysis of a sample of GK-331 enamel with different added Fe_2O_3 content, wt.%: *1*) no Fe_2O_3 addition; *2*) 9% Fe_2O_3; *4*) 15% Fe_2O_3.

Electrochemistry at the Urals Branch of the Russian Academy of Sciences. An x-ray diffraction experiment was performed by the standard procedure of obtaining powder diffraction patterns. Line width is determined by the number of components.

As follows from Fig. 3, the area of the amorphous halo decreases as the added content of iron oxide Fe_2O_3 increases from 0 to 15 wt.%. It can be concluded from the results of x-ray phase analysis that structural rearrangement occurs with increasing mass fraction of iron oxide in the enamel samples. The low accuracy of the measurements makes it possible to uniquely characterize the glass – crystal phase transition, which definitely appears in local sections of the glass phase. For high Fe_2O_3 concentrations the elevated mobility of the silicon-oxygen groupings surrounded by iron cations effects their rearrangement into a crystalline phase possessing the minimum energy.

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